

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) IMPROVEMENTS IN DIAMOND COMPACTS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to polycrystalline diamond compacts and to a process for preparing such compacts.

Polycrystalline diamond compacts possess considerable potential importance for use as a commercial abrasive material. A number of such compacts have been disclosed, bonded by any one of a variety of matrix materials or, in some cases, bonded directly to each other at very high pressures and temperatures. Such compacts have not, however, achieved any commercial importance principally because of strength deficiencies.

Polycrystalline diamond also exists in nature in the form of carbonados. Such carbonados are impure aggregates of single-crystal diamonds held in a matrix of materials which ordinarily occur in the crust of the earth in which the carbonados are found. Thus carbonados generally have as impurities silicate minerals or metals such as aluminium, copper, manganese, chromium, nickel, titanium, iron and magnesium, usually in compound form, in quantities ranging from a trace amount to several percent by weight of the total diamond aggregate. These natural diamond aggregates are, however, relatively scarce and, in addition, their structure and properties are non-uniform from aggregate-to-aggregate and non-homogeneous within a given aggregate. An analysis of different portions of the same carbonado will disclose different constituents, densities and strength properties. While, there-

fore, such carbonados are a useful article of commerce, their utility has been seriously restricted by both their scarcity and the non-uniformity of their characteristics and properties.

It has now been discovered that polycrystalline diamond compacts differing in certain important aspects from the carbonados found in nature and possessing outstanding strength properties may be prepared by subjecting a plurality of boron-doped diamond crystals to a pressure in excess of 50 kilobars, preferably from 50 to 100 kilobars, and a temperature in excess of 1300°C., preferably from 1300 to 3100°C.

Boron-doped diamond crystals may be prepared by subjecting carbonaceous material such as graphite to pressures above 40 kilobars and temperatures above 1200°C. in the presence of boron or a boron compound with a catalyst metal, as more fully described in U.S. patent 3,148,161. Alternatively, boron may be diffused into a diamond crystal by subjecting the crystal to pressures above 8500 atmospheres and temperatures above 1300°C. in the presence of boron or a boron compound, as more fully described in U.S. patent 3,141,855. Boron-doped diamond may also be prepared, directly and in the absence of a catalyst, at relatively higher pressures of 130 kilobars or more. The particular method by which the diamond crystal becomes doped with boron forms no part of the present invention. It is only necessary that a boron-doped diamond be used, and preferably a diamond crystal containing from 0.01-0.5% by weight boron. The latter percentages have been found to produce the highest strength compacts.

The boron-doped diamonds are compacted and bonded preferably in a high-pressure, high-temperature apparatus of the type used in the synthetic production of single-crystal diamond. Diamond compacts

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so produced have uniformly high properties, both from compact to compact and within the same compact. In addition, they exhibit shear strengths of 50,000 to 130,000 pounds per square inch. This is equal to or greater than the range of strengths measured for good quality single crystals of natural diamond or good quality carbonados. The compacts possess a density greater than 3.2 grams per cc., which is in excess of 91% of the theoretical density of single-crystal diamond.

The invention will be more clearly understood from the following description taken in connection with the accompanying drawing in which the single figure is a sectional view of a reaction vessel for use in a high-pressure, high-temperature apparatus which may be used for producing the polycrystalline diamond compacts of the invention.

In our copending application 36801 of 1968 (Serial No. 1240525), a method of preparing polycrystalline diamond compacts is described in which the diamond crystals are preliminarily heated or, alternatively, bombarded with positive ions prior to compaction at high pressures and temperatures. It is believed that this preliminary treatment produces diamonds having a surface which is modified and which is free of solid or gaseous films which would otherwise inhibit bonding. While such a preliminary treating step may also be used in the practice of the present invention, it has been surprisingly found that it is generally unnecessary, and that compacts having properties equivalent to or better than those of our copending application 36801/68 (Serial No. 1240525), may be prepared without such a preliminary step if boron-doped diamonds are used.

The sintering and compacting of the doped diamond crystals of this invention is preferably carried out at a pressure of 65 kilobars or higher and a temperature of 1500° - 1800°C., for periods of time ranging from 10 to 30 minutes. One suitable apparatus for carrying out the sintering operation is disclosed in U.S. patent 2,941,248 - Hall. A reaction vessel suitable for use with an apparatus of the type shown in the Hall patent and which may be used for preparing polycrystalline diamond compacts in accordance with the present invention is shown in the drawing. The reaction vessel 1 is of the so-called indirectly heated type having a pyrophyllite outer cylinder 2, a graphite heating tube 3 placed concentrically within 2 for indirectly heating the sample to be subjected to the high-temperature-pressure operation. A further cylinder 4 of alumina is placed within the graphite heater tube 3, and finally a graphite inner liner 5 is placed within the alumina. Graphite end plugs 6 and 6' and alumina end plugs 7 and 7' fit within the upper and lower portions of the

graphite inner liner and the alumina cylinder respectively to support, shield and insulate the components of the reaction vessel. In a typical compacting operation, boron-doped diamond crystals are manually packed into the graphite-lined, indirectly heated sample holder shown in the drawing, and sintered at pressures of 65 to 70 kilobars at a temperature of 1800°C. As a result of the application of high pressure, the diamond particles are fractured, thus exposing fresh, clean surfaces which are more readily bondable.

Our experiments indicate that the sintering operation is best performed in an inert container or preferably one in which a reducing atmosphere is present during the sintering. For this reason, we have chosen a graphite-lined reaction vessel. If the graphite liner 5 is not present and the particles to be compacted are in contact with the alumina 4, it has been found that a compact of lower strength will result. The reason is that the alumina provides a source of oxygen to recontaminate the diamond, preventing a good diamond-to-diamond bond, whereas graphite is a good getter for oxygen and tends to maintain the atmosphere in the reaction vessel reducing during the sintering process. There are alternate schemes to do this, such as providing a titanium getter or a metal of similar characteristics. Furthermore it has been found that it is important to shield the diamond from contamination while sintering. The alumina liner plus the graphite liner, separately and in combination, provide shields for the diamond from decontamination products of the heated pyrophyllite stone. Other shields or barriers could be used in place of the above materials or in addition to them, such as capsules of refractory metals like tantalum, tungsten, molybdenum, titanium or zirconium.

The pressures which should be used in preparing the compacts of the invention are based upon a calibration procedure which is related to known electrical resistance changes of various metals at room temperature under known pressures as described and illustrated in the aforementioned U.S. patent 2,941,248 and as modified by correcting the calibration as described in "Calibration Techniques in Ultra-High Pressure Apparatus", F.P. Bundy, Journal of Engineering for Industry, May, 1961, Transactions of the ASME, Series B.

The diamond particles from which the compacts are made should have a size of preferably less than 100 microns, and even more preferably a size less than 20 microns. The specific micron size of the diamond particles selected will, of course, be dependent on the application intended for the polycrystalline diamond compact. It is desirable to use a mixture of particle sizes to

facilitate high initial packing densities according to known procedures. In many instances, it may be necessary to clean the diamond powder chemically prior to subjecting it to the high pressure-temperature compaction operation. Such chemical cleaning may be performed by means well known in the art, as for example by the use of hydrochloric acid or aqua regia or by other acid treatment.

The diamond may be compacted, if desired, in conjunction with a small amount of an additive material, either in the form of a matrix or a coating on the diamond crystals. Among the matrix materials which may be used are boron, tantalum, molybdenum, and titanium or their carbides and borides. For example, boron carbide ( $B_4C$ ) may be used in amounts from 0.2 to 0.8% by weight, boron in amounts ranging from about 0.1 to 0.6%, or titanium boride ( $TiB_2$ ) in amounts ranging as high as 1% by weight of the polycrystalline diamond compact. Molybdenum, titanium, nickel and their alloys are illustrative coating materials. However, the compacts should not contain in excess of 2% by total weight of the compact of material other than diamond. Compacts containing more than 2% of such material do not possess the requisite strength properties.

Claim 7 of co-pending application 36801 of 1968 reads as follows:—

"7. A high-strength coherent polycrystalline diamond compact consisting essentially of a plurality of fine diamond particles and no more than 2% by weight of material other than diamond, said compact having a density in excess of 91% of the theoretical density of diamond, the structure and density of said compact being homogeneous throughout."

#### WHAT WE CLAIM IS:—

1. A high-strength, coherent polycrystalline diamond compact consisting essentially of a plurality of boron-doped diamond particles which particles contain at least 0.01% boron by weight; said compact containing no more than 2% by weight of material other than diamond, such material if any being boron, tantalum, molybdenum, titanium and carbides of these elements; said diamond compact having a density in excess of 91% of the theoretical density of single-crystal diamond.

2. A diamond compact according to Claim 1 in which the diamond particles are of less than 20 micron size.

3. A process for producing polycrystalline diamond compacts comprising compacting boron-doped diamond crystals at a pressure in excess of 50 kilobars and a temperature in excess of 1300°C. to form a high-strength, coherent polycrystalline diamond compact. Said compact containing no more than 2% by wt of material other than diamond, such material, if any, being boron, tantalum, molybdenum, titanium and carbides of those elements.

4. A process according to Claim 3 wherein the compacting step is performed in a reducing environment shielded from contamination.

5. A diamond compact as claimed in Claim 1 substantially as described.

6. A process for producing diamond compacts as claimed in claim 3 substantially as described.

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1 SHEET

COMPLETE SPECIFICATION

This drawing is a reproduction of  
the Original on a reduced scale.

